Glass and Ceramics, Vol. 68, Nos. 7 – 8, November, 2011 (Russian Original, Nos. 7 – 8, July – August, 2011)

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.76

ZrO_2 – Al_2O_3 CERAMIC WITH EUTECTIC ADDITIVES

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Translated from *Steklo i Keramika*, No. 8, pp. 23 – 27, August, 2011.

It is shown that the principles of directed control of structure formation in materials by adding eutectic to modify their compositions are valid not only for aluminum oxide based ceramic, but also for ZrO_2 based ceramic materials. The approaches considered for creating energy- and resource-efficient technologies serve as a reliable base for intensifying technological processes, lowering production costs, and increasing product quality. A material with a fine crystalline structure, ultimate bending strength 800 ± 30 MPa, and sintering temperature 1500°C and holding promise for use in construction has been developed in the system CaO – ZnO – Al_2O_3 – SiO_2 on the basis of zirconium dioxide by introducing corundum and eutectic additive.

Key words: zirconium dioxide, aluminum oxide, eutectic, resource efficiency, sintering temperature, mechanical strength.

The system Al_2O_3 – ZrO_2 is fundamental for a host of construction materials. Specifically, it is promising for the manufacture of the friction pairs of a cutting tool. In this country hard-alloy cutting materials are often used for such tools. However, a ceramic tool has a thinner cutting edge (0.1 – 0.2 μm, while for metal 0.7 – 0.8 μm) and 7 – 10 times longer service life with no sharpening, and it permits cutting at high speeds. It is believed that the ultimate bending strength of such a ceramic should be not less than 800 MPa.

One of the most important problems zirconium ceramic technology is that zirconium dioxide rapidly recrystallizes at temperatures above 1100 – 1200°C. As a result of this phenomenon, crystals of a tetragonal solid solution are larger than the critical size and a martensite transformation, accompanied by a substantial drop in the mechanical strength, occurs [1]. An effective method of preventing recrystallization is to apply an external compressive load on the zirconium dioxide grains. Such a load can be produced by introducing into the composition of the material a second phase; aluminum oxide is given this role. Likewise, it is important that the corundum itself not be subjected to intense recrystallization, since crystal growth can cause pores to become trapped and the mechanical strength to decrease.

The sintering temperature of such materials is 1600 – 1650°C, so that new energy-efficient technologies are need for such ceramic.

The objective of the present work is to develop ceramic materials in the system Al_2O_3 – ZrO_2 with zirconium dioxide predominating, which have sintering temperatures 1500 – 1550°C and are characterized by ultimate bending strength at least 800 MPa.

To solve this problem an attempt is made to lower the sintering temperature on the basis of the principles adopted in the aluminum oxide based ceramic technology, i.e., by modifying the composition of the materials using eutectic compositions as additives [2, 3]. A modifying agent in the system CaO – ZnO – Al_2O_3 – SiO_2 was used to control the structure and properties of the ceramic. Aside from this, the effect of different kinds of aluminum oxide (commercial — Al_2O_3-G and obtained by chemical precipitation from chloride — Al_2O_3-Ch) on the properties, mechanical strength, and microstructure indicators of the ceramic.

The initial compositions contained 3 and 4%[3] eutectic additive CaO – ZnO – Al_2O_3 – SiO_2. The kilning temperature was varied from 1400 to 1550°C with step 50°C. The results of these studies are presented in Table 1.

For material containing 10% Al_2O_3-G, as the kilning temperature increases to 1500°C, the lineal shrinkage $\Delta l/l$ and average density ñ increase while open porosity P_0 decreases. An increase of the temperature to 1550°C with 3% and 4% sintering additive introduced decreases the average density considerable and increases the open porosity. Ceramic containing 3% eutectic additive has a higher average

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[3] Here and below, unless stipulated otherwise, the content by weight.

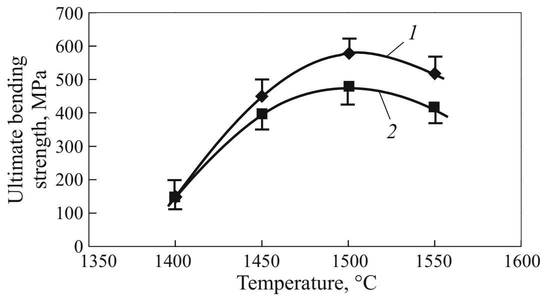

Fig. 1. Mechanical strength of samples containing 10% Al_2O_3-G: eutectic additive 3% (*1*) and 4% (*2*).

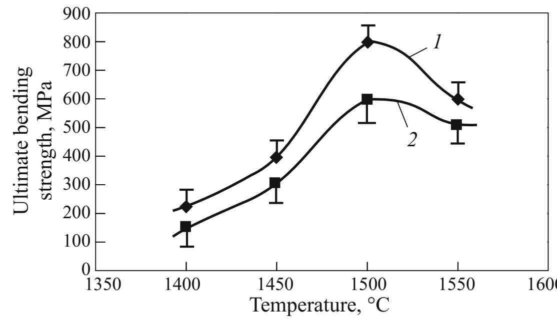

Fig. 2. Mechanical strength of samples containing 20% Al_2O_3-G: eutectic additive 3% (*1*) and 4% (*2*).

density, but the open porosity and lineal shrinkage turn out to be practically the same. For the experimental amounts of the modifying agent, the materials containing 10% Al_2O_3-G sinter to a dense state at temperature 1500°C.

Analyzing the trends in the variation of the open porosity as a function of temperature for ceramic containing 20% Al_2O_3-G, it should be noted that they are identical to those for materials containing 10% aluminum oxide: for the experimental amounts of eutectic added they likewise sinter to a dense state at temperature 1500°C.

Thus, the introduction of 4% sintering additive has practically no effect on the change in the properties of ceramic as compared with materials containing 3% $CaO - ZnO - Al_2O_3 - SiO_2$ additive.

The mechanical strength of the samples containing 10 and 20% Al_2O_3-G is presented in Figs. 1 and 2. Irrespective of the amount of the modifying additive with 10% Al_2O_3-G, a peak at kilning temperature 1500°C is observed in the curves. Other conditions being equal, the materials containing 3% eutectic additive have a higher density.

The variation of the strength properties of ceramic with 20% Al_2O_3-G trends similarly. The material containing 3% additive of the eutectic composition and kilned at temperature 1500°C has the highest mechanical strength — 800 ± 30 MPa. Increasing the kilning temperature from 1500 to 1550°C will decrease the average ultimate bending strength.

The properties of ceramic synthesized using aluminum oxide obtained by chemical precipitation are presented in Table 2. For material containing 10% Al_2O_3-Ch, in contrast to ceramic with Al_2O_3-G, as the kilning temperature is increased the lineal shrinkage and average density increase and the open porosity decreases. Other conditions being equal, the material containing 3% eutectic additive is characterized by higher open porosity.

For the experimental amounts of the eutectic additive the materials with 10% Al_2O_3-Ch sinter to a dense state at temperature 1550°C. For all practical purposes, the introduction of 4% sintering additive does not change the properties of the ceramic as compared with material containing 3% $CaO - ZnO - Al_2O_3 - SiO_2$ additive. The only difference is lower open porosity for materials with a large quantity of sintering additive, which, however, does not greatly affect the sintering temperature.

TABLE 1. Sintering Indicators for Ceramic Containing 10 and 20% Al_2O_3-G and Additive of Eutectic Composition $CaO - ZnO - Al_2O_3 - SiO_2$

Kilning temperature, °C	Properties of ceramic containing additive $CaO - ZnO - Al_2O_3 - SiO_2$ in amounts, wt.%					
	3.0			4.0		
	$\Delta l/l$, %	ρ, g/cm^3	P_0, %	$\Delta l/l$, %	ρ, g/cm^3	P_0, %
			10% Al_2O_3-G			
1400	13.2	4.52	16.6	12.6	4.44	17.0
1450	18.0	5.22	7.2	18.6	5.17	7.7
1500	19.6	5.43	0.0	19.6	5.37	0.0
1550	19.4	5.14	1.6	19.4	5.06	1.5
			20% Al_2O_3-G			
1400	12.0	4.27	17.9	12.0	4.23	18.0
1450	17.3	4.83	10.8	17.1	4.79	11.5
1500	19.6	5.18	0.0	19.6	5.16	0.0
1550	19.4	5.40	0.9	19.4	5.40	1.4

TABLE 2. Sintering Indicators of Ceramic Containing Al_2O_3-Ch and Additive of Eutectic Composition in the System $CaO - ZnO - Al_2O_3 - SiO_2$

Kilning temperature, °C	Properties of ceramic containing additive $CaO - ZnO - Al_2O_3 - SiO_2$ in amounts, wt.%					
	3.0			4.0		
	$\Delta l/l$, %	ρ, g/cm^3	P_0, %	$\Delta l/l$, %	ρ, g/cm^3	P_0, %
			10% Al_2O_3-Ch			
1400	11.5	4.52	18.8	11.8	4.48	18.3
1450	16.5	4.80	13.5	17.5	4.88	11.8
1500	19.2	5.17	7.0	19.2	5.19	5.8
1550	20.0	5.44	0.0	20.0	5.38	0.0
			20% Al_2O_3-Ch			
1400	10.5	4.22	20.0	11.2	4.20	19.0
1450	15.4	4.52	12.8	17.0	4.54	11.4
1500	18.1	4.92	3.3	18.3	4.92	2.3
1550	18.9	5.19	0.0	19.0	5.15	0.0

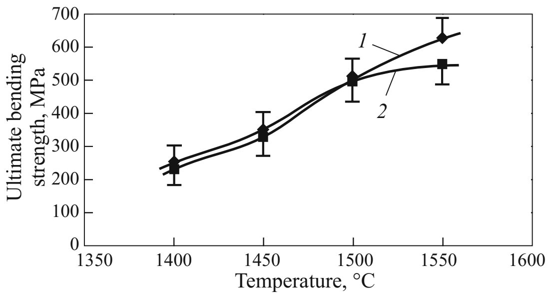

Fig. 3. Mechanical strength of samples containing 10% Al_2O_3-Ch: eutectic additive 3% (*1*) and 4% (*2*).

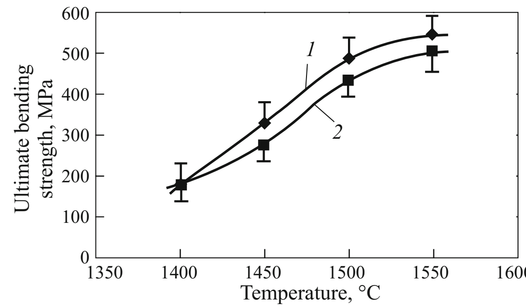

Fig. 4. Mechanical strength of samples containing 20% Al_2O_3-Ch: eutectic additive 3% (*1*) and 4% (*2*).

Analyzing the trends in the variation of the open porosity as a function of temperature for ceramic containing 20% Al_2O_3-Ch, it should be noted that they are identical to those for the material with 10% aluminum oxide.

Other conditions being equal (kilning temperature, amount of sintering additive), the open porosity decreases with increasing Al_2O_3-Ch content. The average density is also found to be lower, mainly because the materials contain larger amounts of aluminum oxide. For the experimental amounts of the eutectic additive, ceramic with 20% Al_2O_3-Ch sinters to a dense state at temperature 1550°C.

Irrespective of the amount of the modifying agent introduced as well as of the aluminum oxide content in the composition, the ultimate three-point bending strength increases as the kilning temperature increases (Figs. 3 and 4).

The ceramic containing 3% eutectic additive and kilned at temperature 1550°C possesses the highest mechanical strength 620 ± 40 MPa.

The microstructure of ceramic based on partially stabilized zirconium dioxide (PSZD) is characterized in Table 3.

Thus, it can be concluded that the best mechanical properties were obtained by introducing 20% aluminum oxide synthesized on the basis of the hydroxide. The use of 10% aluminum oxide does not prevent recrystallization of zirconium dioxide. Growth of crystals of the solid solution lowers the mechanical strength. Twenty percent Al_2O_3 is adequate to prevent recrystallization of the solid solution completely (see Table 3).

It was established that in materials with a large amount of low-melting component there is no common boundary between the zirconium dioxide grains. This results in a large decrease of strength. So, the average ultimate bending strength is 800 ± 30 MPa with the introduction of 3% modifying agent and 20% Al_2O_3-G and 680 ± 40 MPa with 4% eutectic. The reason for this phenomenon is the absence of a common boundary between the particles. Thus, the amount of the low-melting component in such a ceramic must be strictly controlled in order to create a direct bond between the zirconium dioxide grains.

Materials with different compositions behave differently as the kilning temperature increases. So, for ceramic containing 10% Al_2O_3-G, as the kilning temperature increases to 1500°C, a regular decrease of the open porosity and increase of the mechanical strength are observed. Increasing the temperature to 1550°C increases the open porosity and decreases the mechanical strength, irrespective of the amount of sintering additive introduced. The latter is due to the negligible decomposition of PSZD and precipitation of the monoclinic modification occurring as a result of the recrystallization.

For ceramic containing 20% Al_2O_3-G as the kilning temperature increases from 1500 to 1550°C the average density

TABLE 3. Microstructure of Ceramic Based on PSZD with $CaO – ZnO – Al_2O_3 – SiO_2$ Additive; Kilning Temperature 1500°C

Additive content, wt.%	Aluminum oxide component		Crystal size, μm		Glass phase content, vol.%	Closed volume porosity, %
	Type	Content, wt.%	ZrO_2	Al_2O_3		
3	Al_2O_3-G	10	2.0 – 4.0	1.0 – 1.5	0	0
4			4.0 – 5.0	1.0 – 1.5	0	0
3	Al_2O_3-Ch	10	2.0 – 4.0	8.0 – 10.0	4 – 5	< 2
4			2.0 – 4.0	8.0 – 10.0	5 – 6	2 – 3
3	Al_2O_3-G	20	1.0 – 1.5	1.0 – 1.5	0	0
4			1.0 – 1.5	1.0 – 1.5	0	0
3	Al_2O_3-Ch	20	1.0 – 1.5	8.0 – 12.0	5 – 7	< 2
4			1.0 – 1.5	8.0 – 12.0	6 – 8	2 – 3

TABLE 4. Comparison of Some Materials of the System Al_2O_3 – t-ZrO_2 Kilned in Air

Parameter	Material			
	ZTA [5]	IPK RAN* [6]	Material developed	MKhTI** [7]
Stabilizer	Y_2O_3	CeO_2	Y_2O_3	Y_2O_3
Al_2O_3 molar fraction	0.80	0.50	0.24	0.00
Pressing pressure, MPa	100	200	100	100
Kilning temperature, °C	1600	1650	1500	1650
Average ultimate bending strength, MPa	600	700	800	1100
Relative density	0.99	0.99	0.99	0.99
PSZD crystal size, no larger than, μm	2.0	2.0	1.5	0.8

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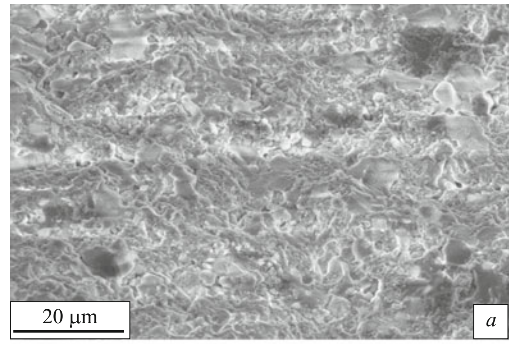
and the open porosity increase simultaneously. A calculation of the true porosity shows that for material containing 3% modifying additive and 20% Al_2O_3-G its equals 5.27 g/cm^3, which is much lower than the density of the ceramic at 1550°C (5.40 g/cm^3).

Petrographic analysis shows that partial decomposition of the tetragonal solid solution occurs in this case, not with the monoclinic phase of zirconium dioxide precipitating but rather the cubic phase, which is why the density of the ceramic increases. The solid solution in this case is represented by the t and t' phases. The latter, with high stabilizer content, decomposes with the stable cubic and metastable t phases precipitating. The likelihood of such decomposition is show in [4]. Because the CLTE of the cubic phase is different from that of the tetragonal phase different microcracking is observed along the boundaries of the crystals of the solid solutions: such microcracks reach < 1 μm in size and their amount reaches 2 vol.%. This is sufficient to increase the open porosity.

Materials into which aluminum oxide synthesized by chemical precipitation is introduced behave completely differently (Table 2). For any amounts of Al_2O_3 and any content of modifying additives in the initial compositions, the mechanical strength increases with increasing kilning temperature.

When aluminum oxide obtained by chemical precipitation is introduced a melt whose composition is different from the eutectic forms in the system. This liquid does not crystallize on cooling, but rather it remains in the form of glass, which degrades the mechanical properties considerably. Extremely intense recrystallization of aluminum oxide is observed for the same reason (deviation of the composition from a eutectic). Increasing the amount of modifier introduced, just as the content of aluminum oxide, increases the



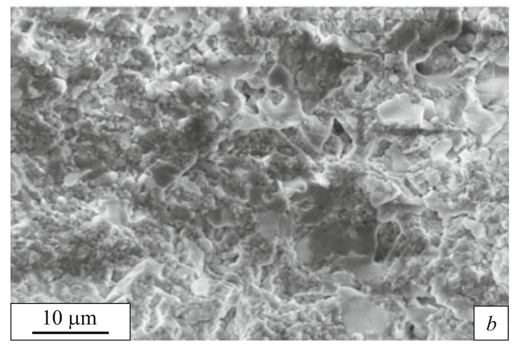


Fig. 5. Microstructure of samples based on zirconium dioxide with additives 3% $CaO – ZnO – Al_2O_3 – SiO_2$ and 20% Al_2O_3-G.

amount of melt and hence also glass in the phase composition of the ceramic (Table 3). Therefore, a composition containing a minimal amount of modifying additives should posses the highest strength; this is observed in practice: the average ultimate bending strength of ceramic containing 3% eutectic additive and 10% Al_2O_3-Ch and kilned at 1550°C is 630 ± 35 MPa.

Such behavior of Al_2O_3-Ch is due to the well-known phenomenon of structure inheritance. The crystal lattice of Al_2O_3-Ch inherited the high-defect structure which the material acquired in the process of precipitation. The defect density is responsible for the high reactivity of aluminum oxide and imparts to it the capability of dissolving in substantial quantities in silicate melt.

Aluminum oxide obtained by calcining the hydroxide has a much lower reactivity, since it is synthesized from the hydroxide with a well-formed crystal lattice. Such structure is also inherited by the synthesized product, i.e., Al_2O_3-G.

Some materials in the system $Al_2O_3 – ZrO_2$, which are promising for durable parts and cutting tools, are compared in Table 4. As follows from the data presented, the strength properties of the material developed are comparable to those of the leading materials synthesized by scientists in this country and abroad. Nonetheless, the sintering temperature of the ceramic developed is much lower.

Photographs of the microstructure of the ceramic with the highest mechanical strength are presented inn Fig. 5.

In summary, it must be concluded that the principles of directed control of the process forming the structure of mate-

rials whose compositions are modified by eutectic additives are valid not only for ceramics based on aluminum oxide and materials containing zirconium dioxide but also for composite ceramic materials based on ZrO_2. The approaches examined here to developing energy- and resource-conserving technologies serve as a reliable foundation for intensifying the technological processes of lowering production costs and increasing product quality.

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